

radiation produced in tungsten and copper and the ionisation resulting in ethyl bromide and nickel carbonyl, when equal amounts of energy of the two radiations were absorbed in the various substances, have been measured, and were found in each case to be independent of the radiator.

The results prove that these two spectra of radiations, Group K and Group L, are identical in their nature, as is shown by measurements on radiations in both groups which test—(1) their absorption in elements; (2) their power of producing corpuscular radiation; (3) their power of ionising. This suggests that the mechanism of production is the same, although the elements emitting the radiation differ widely in atomic weight.

I wish to express my best thanks to Sir J. J. Thomson for his interest and advice throughout this research.

The Synthesis of a Silicalcyanide and of a Felspar.

By J. EMERSON REYNOLDS, M.D., Sc.D., F.R.S.

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[PLATE 1.]

In the course of an investigation which has occupied much time during some years the writer has obtained a considerable number of definite compounds including silicon and the nitrogen of diverse organic groups in direct chemical union. Several of these new substances resemble in composition and in their general relations certain well-known compounds of carbon with nitrogen, such as amides, imides, and nitriles, among them being a silicocyanogen group, SiN, in combination. The formation of such substances afforded complete proof that silicon has, like carbon, though in less degree, a marked affinity for trivalent nitrogen, even when the latter is associated with complex organic groups.*

* These substances have been described in detail in the 'Transactions of the Chemical Society' in the following papers:—"The Action of Silicon Tetrabromide on Thiocarbamide," 'Chem. Soc. Trans.,' vol. 51, p. 202; "The Action of Silicon Tetrabromide on Allyl and Phenylthiocarbamides," vol. 53, p. 854; "The Action of Ethyl Alcohol on the Compound $(H_4N_2CS)_3SiBr_4$," vol. 53, p. 868; "On Silicotetraphenylamide, *para*- and *ortho*-Silicotetratolylamides, α - and β -Silicotetranaphthylamides," vol. 55, p. 474. These compounds were the first of those obtained in which silicon is exclusively united with nitrogen and forming crystalline substances. "The Action of Substituted Phenylamines on Silicon Tetrachloride," vol. 61, p. 453; "On Silicodiphenyldiimide and Silicotriphenylguanidine," vol. 77, p. 836; "The Bromination of Silicophenylimide and -amide, and the

In the mineral kingdom no definite compounds of silicon with nitrogen have yet been met with ; nor are they likely to be found at any part of the earth's surface to which water has easy access, as it is probable that any such substances would be very speedily decomposed in presence of moisture into silica and ammonia, or their derivatives. On the other hand, the existence of the great group of "alumino-silicates," which constitute so large a proportion of granitic and other similar rocks, affords clear evidence of the strong attraction of silicon for aluminium, which latter acts as an essentially trivalent element in its high temperature relations, and seems capable under such conditions of doing chemical work somewhat similar to that of nitrogen. These considerations raised the question whether some at least of the alumino-silicates may not be regarded as fully oxidised products of silicides of trivalent aluminium, somewhat analogous to SiN , which had been formed at high temperatures in the first instance below the oxidised crust of the earth. It is evident that such "nuclear" silicides should be obtained for study by the complete deoxidation of the corresponding native silicates, or by direct synthesis from the suitable elements. The first method was found to be impracticable in the most important cases, *i.e.* of alumino-silicates including alkali or alkaline earth metals. The application of the second or synthetic method has proved satisfactory, as it has led to the discovery of a substance of remarkable stability, provisionally named Calcium Silicalcyanide, and with which a new synthesis of the felspar Anorthite has been effected. The results recorded in the following pages tend to support the view suggested above as to the nitrogen rôle of aluminium in certain silicides, and afford some further clues to the constitution and natural relations of the plagioclasic feldspars.

Experimental Part.

The *reduction*, or deoxidation, of silica and alumino-silicates is easily effected by several agents ; but the most convenient of these is metallic magnesium. It is well known that the finely divided metal when heated with silica (SiO_2) in suitable proportions readily removes all the oxygen of that substance, so that elemental silicon and magnesium oxide result, and the latter can then be removed by hydrochloric acid, in which silicon is insoluble. All the "alumino-silicates" which I have treated in the same manner are also reduced, but not completely ; for example, anorthite,

formation of a Compound including the Group SiN ," vol. 87, p. 1870 ; "On Interactions of Silicotetraphenylamide and Thiocarbimides," vol. 88, p. 252 ; "On Silicon Thiocyanate : its Properties and Constitution," vol. 89, p. 397 ; "On Silicotetrapyrrole," vol. 95, p. 505 ; "The Action of Potassium-pyrrole on Silico-chloroform," vol. 95, p. 508 ; and "Silicon Halides with Pyridine, Acetonitrile, etc.," vol. 95, p. 513.

oligoclase, orthoclase, and scapolite, when heated with the proportion of magnesium suitable for the removal of the whole of the oxygen in each case, gave nearly black reduction products. These were closely examined and found to be slightly coherent masses which did not afford any metal-like particles when broken up. Treated with cold water, no gas was evolved, and very little even on boiling; but the alkalies present in any of the minerals were not deoxidised, and dissolved in the water, along with much of the lime from anorthite and scapolite. The alkaline substances were washed away and the black insoluble residue, which still contained magnesia but no visible traces of metal, was in each case treated with hydrochloric acid; some hydrogen was given off, and the colour of the powder changed to the well-known brown of finely divided and amorphous silicon, while aluminium and magnesium passed into solution.

In all these cases it was evident that the chief effect was reduction to silicon with more or less of a black silicide of aluminium, which latter was subsequently decomposed by the acid—a further proportion of silicon separating. The reduction method, therefore, only partially attained the end in view; hence, attention was next given to the second line of treatment.

The *synthetic* method consisted in attempts to combine the unoxidised elements under well defined conditions, and to study any definite products obtained.

On the hypothesis already suggested, that aluminium can, in certain cases, act in regard to silicon in inorganic nature much as nitrogen does to carbon in the organic division, we should expect the following series of compounds to exist:—

Cyanogen	C_2N_2 or $(CN)_2$
Silicocyanogen	Si_2N_2 or $(SiN)_2$
Silicalcyanogen.....	Si_2Al_2 or $(SiAl)_2$

We know that the first term of this series—ordinary cyanogen gas—is formed with difficulty from its elements except at very high temperatures, but much more readily in presence of a third and more positive substance, such as an alkali metal, which can directly combine with cyanogen as it is formed and produce a cyanide. The second term is not known in the free state, unless it is the white substance which is produced when silicon is heated to the temperature of the electric arc in an atmosphere of nitrogen; but I have obtained the group SiN in organic combination. The third term has not been recognised hitherto either in the free state or in combination. It seemed probable, however, that Si_2Al_2 might be more easily formed by direct union of the elements than the others, because both are fusible solids; hence the first experiments were directed to this point.

It is well known that silicon dissolves freely in molten aluminium at moderately high temperatures, but that much of the former separates in crystals on cooling. Winckler found that when the liquid from which excess of silicon had crystallised out and been removed was allowed to solidify, it consisted of nearly equal parts of silicon and aluminium. As the atomic weights of the elements are $\text{Si} = 28.3$ and $\text{Al} = 27.1$, Winckler* was disposed to regard this "alloy" as a definite compound, and therefore to be represented by the formula SiAl . On the other hand, Vigouroux† denies that any definite compound is formed when aluminium and silicon are fused together. Fraenkel,‡ also, concludes from his thermochemical observations that there is little or no chemical combination. The following experiments were made with a view to examine this point more closely.

100 grms. of the purest commercial aluminium were fused in a "salamander" crucible, and 104 grms. of graphitic silicon were added in small fragments to the molten metal. There was no evidence of chemical action after each addition nor as the silicon slowly dissolved. When complete solution was obtained the liquid was heated to full redness for half an hour, and the crucible with its contents were then allowed to cool slowly. An apparently homogeneous grey metallic mass was broken out of the crucible which had but slightly oxidised at the surface exposed to the air. A horizontal section made through the middle of this mass showed that the bright metallic surface was crossed by numerous long crystals. A section of about a centimetre in thickness was half immersed in much diluted hydrochloric acid for a day, and deep etching was obtained owing to solution of aluminium. The long crystals which were left in relief, as shown in fig. 1, were found to consist of silicon only. It will be seen, however, that a few crystalline and brilliantly reflecting plates are present in addition to the silicon crystals. Some of these plates were carefully picked out and treated with much stronger acid than that used in etching; the plates disintegrated, leaving pulverulent silicon, while aluminium dissolved. These plates probably represent traces of combination between the two elements.

I next sought to ascertain the composition of the material in which the silicon crystals were embedded. For this purpose a moderately thin section of the large mass, weighing some 30 grm., was supported on edge in a bath of melted calcium chloride, which fuses between 717° and 723° (Carnelly), or a little above the melting point of aluminium, *i.e.* about 700° . Gradual liquation of the aluminium occurred and much crystalline silicon was left. When cold

* 'Journ. für Praktische Chemie,' vol. 91, p. 193.

† 'Comptes Rendus,' vol. 141, p. 951.

‡ 'Zeits. für Anorg. Chemie,' 1908, vol. 58, p. 154.

the metal-like product resembled aluminium in colour but was quite crystalline in structure throughout. The composition proved to be—

Silicon	28.33
Aluminium	71.57
	<hr/>
	99.90

This product when treated with acid also left crystals of silicon.

The original mass contained 50.8 per cent. of silicon, and a portion of this when remelted and suddenly cooled gave a good ingot which was steel-grey in colour, and the fractured surface presented the minutely crystalline structure shown in fig. 2. A portion of the same ingot was again fused and maintained at a full red heat for nearly two hours and then slowly cooled as in the first instance. A section of this product when etched presented much the same appearance as in fig. 1, save that the plates already referred to seemed to be rather more numerous, as if the prolonged fusion had promoted a little further combination of silicon with aluminium.

It is evident that silicon and aluminium do not directly enter into chemical combination to any material extent, even when a liquid mixture in atomic proportions is heated to full redness for more than two hours. Under similar conditions carbon and nitrogen do not evince any greater tendency to unite and form cyanogen; but, in the latter case, if a third element be present, such as an alkali metal, then combination takes place and a cyanide of the metal is formed. On the "silicalcyanogen" hypothesis I have suggested, the addition of an alkali metal, or its equivalent, to the fused alloy of silicon and aluminium should act in a similar manner and lead to the formation of a silicalcyanide of the metal.

A number of prospecting experiments were next made with the molten alloy of silicon and aluminium in atomic proportions, in which sodium, potassium, magnesium and calcium were added to separate parts of the fused alloy. The alkali metals proved to be much too volatile for use in open crucibles*; magnesium dissolved quietly in the alloy without affording much evidence of chemical combination either in process or product; but calcium caused almost violent action as it dissolved in the SiAl alloy, and afforded a very characteristic product. Further experiments having indicated the best conditions for a preparation on a comparatively large scale, this was made in the following manner:—

100 grms. of the purest aluminium obtainable in commerce were fused in a relatively large-sized crucible, heated in a powerful gas blast furnace;

* It will be shown later on that in closed vessels union can be effected to a certain extent.

103 grms. of crystalline silicon, as free as possible from carbide, were introduced, and the heat was continued until complete liquefaction was obtained; 74 grms. of metallic calcium, cut into small pieces, were then gradually added to the molten alloy; each piece, when pressed under the surface of the liquid, caused energetic action, and after the latter had somewhat subsided the liquid was well stirred with a steel rod. Owing to this frequent stirring it was easy to note that the mass became sensibly less fluid after the addition of about half the calcium, as if owing to the separation of less fusible material, and this thickening increased until the last addition was made, when it became nearly solid.* The temperature was then raised to the highest point attainable during half-an-hour, but without fusion, and the whole was then allowed to cool very slowly.

When cold the crucible was broken away and a clean metal-like mass of a dark grey colour was extracted. This weighed 279 grms.—the small increase in weight, about 2 grms., being doubtless due to some oxidation during the vigorous interaction which took place on the addition of the calcium. All traces of free aluminium had disappeared.

A vertical section through the mass presented smooth metal-like surfaces with markings indicative of crystal sections, and the material, which could be easily broken up by a hammer, presented a highly crystalline structure and seemed to be uniform in character. The brilliant crystalline faces appeared to belong to octahedral forms, and to be of the same kind throughout the mass; but at certain parts a dark powdery substance was found which evidently consisted of the mixed oxides already referred to, as having been formed in small quantity at the surface, and then become entangled during the final stirring of the somewhat thick alloy; this powder, which owed its dark colour to mixture with the finely divided portions of the alloy, was easily brushed away, and the broken product then presented the appearance shown in fig. 3.

Some of the best defined crystalline groups were taken from different parts of the mass and their densities determined at 16° in water, which does not sensibly act on the alloy at ordinary temperatures, unless after long contact.

Upper section	2·347
Middle „	2·351
Lower „	2·353

As the densities of the constituents varied between 2·71 for aluminium and 1·534 for calcium, there had not been any material separation, so confirming the essentially homogeneous character of the “alloy.”

* The proportion of calcium added was then nearly $\text{Ca} : \text{Si}_2 : \text{Al}_2$.

Notwithstanding the above evidence, and the known weights of the elements used in the preparation of the alloy, analysis was considered desirable, hence rather large portions were broken from about the middle of the mass; these well crystallised specimens were brushed free from scoria and then finely powdered. The method of analysis consisted in heating the substance, spread in a thin layer on a porcelain boat contained in a Jena glass tube, in a current of carefully dried chlorine gas. The powder was soon attacked and the constituents were converted into chlorides; calcium chloride, not being volatile, was left in the boat when aluminium and silicon, as chlorides, were volatilised by heat and the vapours wholly absorbed by water; Si and Al were then separated in the usual manner. The results of two analyses so conducted are given below, and are compared with the composition of a compound consisting of CaSi_2Al_2 .

	Theory.	I.	II.
Silicon	37·63	36·81	36·76
Aluminium	35·92	—	35·8
Calcium	26·45	25·72	25·86
	100·0		

The slight oxidation which occurred during the preparation of the substance, as already explained, is doubtless the chief cause of the lower values obtained for silicon and calcium than those required by the formula.*

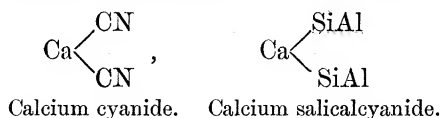
The indifference of this substance to oxygen, even at comparatively high temperatures, is as remarkable as its infusibility. In a special experiment, 2 grms. of the metal-like material, in a rather finely powdered condition, were strongly heated in a porcelain boat placed in a hard glass tube, through which a current of dry oxygen was passed for an hour, while the temperature was maintained as near as was safe to the softening point of the containing tube. The powder did not fuse, and was very slightly altered in appearance; when cold it was found to have gained only 0·08 gm. in weight. When heated in air by the oxyhydrogen flame, the "alloy" melts, and immediately bursts into vigorous combustion, affording a white semi-fused product.

The substance is also remarkable in that water acts very slightly upon it at ordinary temperatures, and little more if boiling, thereby proving

* Numerous silicides and alloys, including aluminium and other elements, have been formed, and are described in the elaborate treatise of M. Baraduc-Muller, 'Sur les Siliciures Metalliques' (Angers, 1910, 4to), but no "alloy" resembling the above either in composition or properties appears to have been obtained.

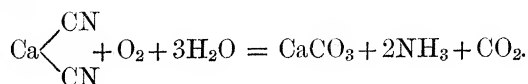
incidentally that the large proportion of calcium which is present is wholly in chemical combination. It is readily attacked, and in part dissolved, by hydrochloric acid, with evolution of hydrogen silicide and free hydrogen, while much silicon separates, aluminium and calcium passing into solution. Strong nitric acid is almost without action in the cold, but the boiling acid slowly attacks the substance; sulphuric acid has little action even when hot. On the other hand, sodium and potassium hydroxides in strong solution act readily in the cold and rapidly on boiling. When dry chlorine is passed over the substance, action begins without the application of external heat, and the products are calcium, aluminium, and silicon chlorides. Advantage was taken of this complete action in order to effect the analyses given above.

The substance presents the essential characters of a chemical compound, and appears to be one which has been formed from its elements much in the same manner that a metallic cyanide can be synthesised, silicon and aluminium representing carbon and nitrogen.* The analogy with a cyanide is easily recognised when the respective formulæ are written as under:—



It has been mentioned above that calcium silicalcyanide is very slightly attacked by free oxygen until the temperature of the oxyhydrogen flame is reached. I may add that even fused potassium chlorate produces little effect upon it, and fused nitre is partial in its action. If heated with easily reduced metallic oxides, such as lead oxide, the compound is broken up, and a lead, calcium, and aluminium glass results from secondary changes.

There is no doubt, however, that the crystalline $\text{Ca}(\text{SiAl})_2$ is capable of combining with eight atoms of oxygen, and of producing therewith a compound of the same composition as the mineral anorthite, that is $\text{CaSi}_2\text{Al}_2\text{O}_8$. Now, ordinary cyanides of alkali or alkaline earth metals are by no means easily affected by gaseous oxygen even at comparatively high temperatures, but, if water vapour be present along with oxygen, change takes place at comparatively low temperatures, resulting in the formation of a carbonate of the metal, while ammonia is formed and separated.† Such a change effected in the case of calcium cyanide can be represented in the following manner:—



* It is possible that barium and strontium may give similar products.

† Unless oxygen is present in excess, when ammonia is oxidised in its turn.

The silicalcyanide should obviously be capable of somewhat similar hydrolytic oxidation, and that proved to be the case, although the inability of aluminium to form a volatile compound like ammonia necessarily led to a modification in the nature of the end product. After several trials the most convenient mode of effecting the change proved to be the following:—

About 2 grms. of the finely powdered alloy were placed in a Rose crucible of rather large size with the usual perforated cover and clay delivery tube for conveyance of gas to the interior. The tube was connected with a flask containing water through which a stream of oxygen was allowed to bubble on its way to the crucible. By heating the water in the flask the proportion of water vapour carried along with the gas could be increased at will, and heating the clay tube prevented condensation before the hot crucible and its contents were reached. Under these conditions the moist oxygen led over the powder, which was heated to low redness, gradually converted it into a nearly white mass. Two successive quantities were treated in the same manner until sufficient of the white product was obtained; the whole was then powdered, returned to the crucible, and again strongly heated in the current of moist oxygen until perfectly white. This material proved to be infusible at the highest temperature attainable in a small gas blast furnace; but when an oxyhydrogen flame was made to impinge on the surface complete fusion was effected of the greater part of the mass; much care was taken to avoid fusing the material of the crucible as well. When slowly cooled in order to permit crystallisation the surface presented the somewhat volcanic appearance shown in fig. 4. Under the crater-like top a good proportion of solid and highly crystalline substance was found.

The best crystallised portions of this product from calcium silicalcyanide were picked out for examination and analysis. When compared with a specimen of opalescent anorthite from the Tyrol my synthetic product proved to be very similar in character, and it was gelatinised by acids in much the same way.

0.962 grm. gave 0.3996 grm. of SiO_2 , 0.3615 of Al_2O_3 , and 0.2045 of CaO .

These data lead nearly to the ratios



or those of the mineral anorthite.

Mr. Herbert H. Thomas, of H.M. Geological Survey, has been so good as to examine a specimen of this product, and kindly allows me to quote his observations, as follows:—"In thin section it presents the appearance of a mass of acicular crystals which radiate from a series of centres; the

individual needles are twinned once in most cases, but in some instances it was possible to make out polysynthetic lamellæ.

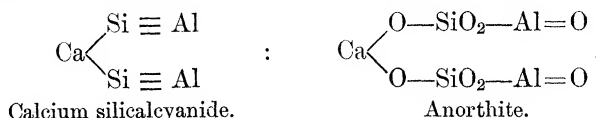
"The powdered mineral has a mean refractive index of about 1·582 and a specific gravity of about 2·75 to 2·76 (heavy liquid method).

"The mineral has low birefringence, large extinction angle on the plane of the best cleavage, and is most certainly a felspar. The high mean refractive index and specific gravity both point with certainty to anorthite."

In the following table the percentage composition of my synthetic* anorthite is compared with theory for the pure substance, and with analyses of native specimens, in order to show the range of variation in composition. For convenience of comparison all the monoxides present in the native minerals have been calculated into their equivalents of CaO and added to the percentages of the latter which were actually obtained. No. 1 is of clear crystals from Monte Somma, analysed by Abich. No. 2 is of the massive variety indianite. No. 3 is of the variety named barsowite, analysed by Friederici:—

	Theory.	No. 1.	No. 2.	No. 3.	New synthetic.
SiO ₂	43·08	43·96	42·09	41·56	41·53
Al ₂ O ₃	36·82	35·72	38·89	36·59	37·3
CaO	20·1	20·26	19·46	21·42	21·25
	100·0				

Whether formed by partially hydrolytic action at comparatively low temperatures, or by direct oxidation alone at much higher temperatures, the relations of calcium silicalcyanide and anorthite are simple, and are expressed in the constitutional formula for the mineral given below:—



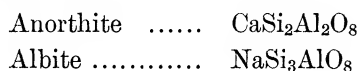
If nitrogen were present in the unoxidised compound instead of aluminium then hydrolysis would have involved its removal as NH₃ gas, and the residue would probably have been a calcium disilicate, which is a potentially acid salt. Anorthite is, on the contrary, a markedly basic silicate, because aluminium does not form any such gaseous compound as NH₃, and in

* The synthesis of anorthite has been effected from the oxides or other compounds of the component elements, but this one is obviously different in character from those which preceded it.

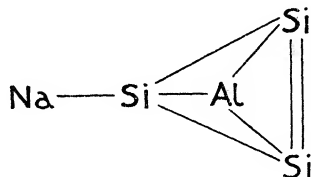
presence of an excess of oxygen, is retained in the molecule as a distinctly electropositive constituent. It is probably owing to the essentially basic character of anorthite that it is so rarely found in the pure state.

According to Tschermac's well-known view, all the plagioclastic felspars are either isomorphous mixtures, or solid solutions, of basic anorthite and the acidic felspar albite in various proportions. These transition minerals are the important rock formers—labradorite, andesine, and oligoclase, with other minor varieties, which exhibit well known and gradual changes in chemical composition and in physical characters between the two extremes.

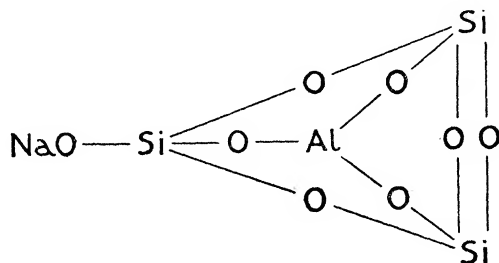
Notwithstanding the wide difference in composition between anorthite and albite, which becomes apparent when the simplest expression of the composition of each mineral is compared as under—



their known relations above mentioned indicate that there is some fundamental similarity in constitution. If the unoxidised nuclei are considered in view of the information gained in the earlier part of this work, it is easy to trace such a relationship. The simple silicalcyanide type underlying anorthite is $-\text{SiAl}$; that of albite is obviously more complex, but still includes at least one such member, if the nucleus be represented by the following constitutional formula :—



Ultimate oxidation of this to albite probably would not make any material change in the relations of the principal elements, and the constitution of that mineral may similarly be represented as under—



It is probable that the free molecule of albite should be represented by two

such groups linked up by the residual valence of aluminium. Orthoclase, KSi_3AlO_8 , may be similar in structure.

The synthesis of albite from the oxides of its component elements is well known to be attended with difficulty; but the synthesis of the corresponding silicide is still more difficult,* owing to the volatility of sodium, and heating under pressure in presence of a considerable excess of sodium is necessary. When the requisite materials were heated in a strong iron tube, closed by a tightly screwed cap, some combination was effected. This tube and its contents, placed in an inclined position in a powerful muffle furnace, was heated to the highest attainable temperature for nearly two hours, and then allowed to cool in sand; when quite cold it was cut into four pieces of nearly equal length. The upper part was lined by some condensed sodium; the next section contained some sodium also, and the third section was found to contain a grey metal-like mass. This was somewhat crystalline in character, quite hard enough to require the use of a chisel in order to cut it out, but the material easily took fire on friction, and when thrown into water gave abundance of hydrogen gas and a little hydrogen silicide. A portion of the grey crystalline alloy was picked out in as clean a condition as possible, and was found to contain silicon, aluminium, and much sodium. It is probably a solid solution of NaSi_3Al in sodium. The lowest section of the tube contained more of the grey alloy and a little free silicon. This alloy is the nearest in the way of an unoxidised albite nucleus that I have as yet been able to obtain.

It is evidently possible that somewhat similar relations may be traceable between alumino-silicides of other types and other classes of "alumino-silicates."

Much of the work recorded in this paper was carried out in the Davy-Faraday Laboratory, and my grateful acknowledgments are due for the facilities afforded by that institution.

* Some chemists, including Deville and Vigouroux, were unable to secure the combination of silicon with sodium or potassium under any conditions; but Moissan, in 1904, easily effected superficial combination by passing the vapour of sodium over silicon at high temperatures.

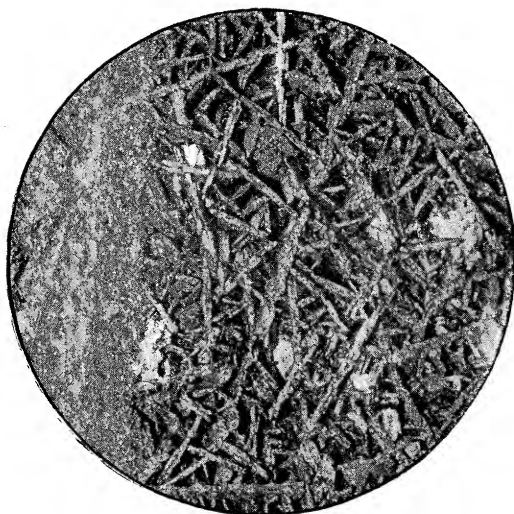


FIG. 1.

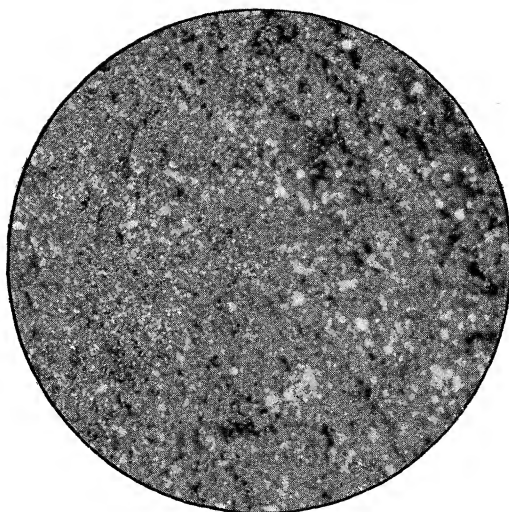


FIG. 2.

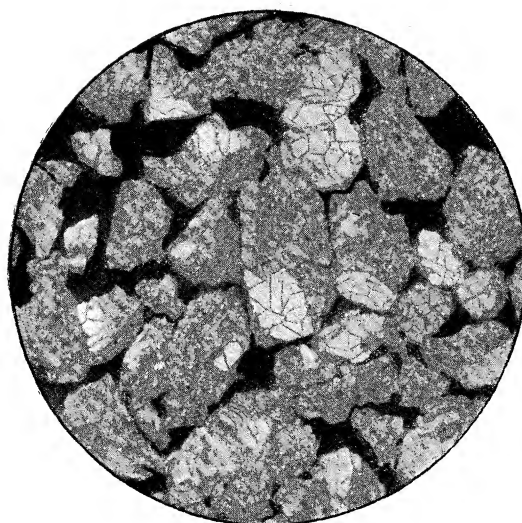


FIG. 3.

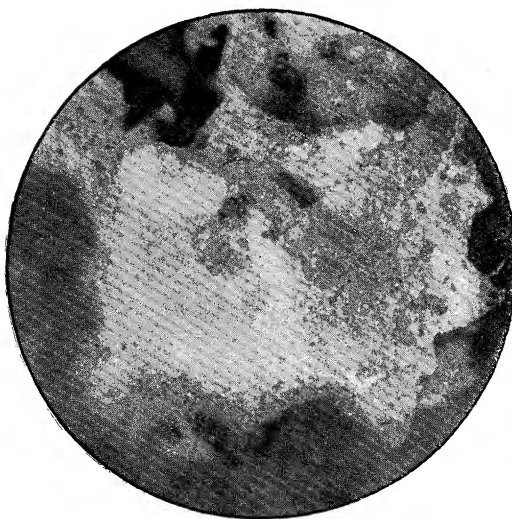


FIG. 4.



FIG. 1.

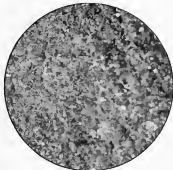


FIG. 2.

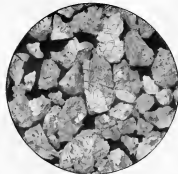


FIG. 3.

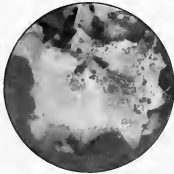


FIG. 4.